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On the Possibility of Mixed Rydberg-Valence Bonds

Alexander I. Boldyrev and Jack Simons*

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

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Chemical bonding between the Rydberg molecule NH_4 and three alkali atoms Li, Na, and K, via their 2s, 3s, or 4s valence orbitals, is examined using flexible atomic orbital basis sets and high level ab initio methods. The results thus obtained suggest that $(NH_4)Na$ and $(NH_4)K$ should have large enough barriers to fragmentation (to (NH_3) plus the alkali hydride) to be detected experimentally if it can be formed, but suggest that $(NH_4)Li$ has such a small barrier to render it impossible or much more difficult to observe. For all three species, minimum-energy structures, local harmonic vibrational frequencies, and plots of the Rydberg-valence bonding orbitals are given. The activation barriers separating these structures from their (NH_4) plus alkali hydride fragments vary from 3 to 9 kcal/mol, while the energies required to dissociate to NH_4 plus an alkali atom range from 9 to 16 kcal/mol.

I. Introduction

Recently we examined[1] the possibility that two Rydberg molecules (NH_4, specifically) could form a two-electron chemical bond via the overlap of their Rydberg orbitals. The NH_4 molecule consists of an underlying closed-shell NH_4^+ cation core with a single unpaired electron occupying a diffuse orbital of a_1 symmetry. Because NH_4^+ is isoelectronic with Na^+, it is common to refer to this a_1 Rydberg orbital of NH_4^+ as a 3s orbital, which is the lowest empty orbital of Na^+. Neutral NH_4 is known to be electronically and locally geometrically stable at this tetrahedral geometry but unstable (by ca. 0.7 kcal/mol[2−7]) with respect to fragmentation to $NH_3 + H$, with a 9 kcal/mol barrier[2−7] restraining this fragmentation. For this reason, one clearly has to consider the possibility that the NH_4 moieties in $(NH_4)_2$ can fragment into $2NH_3 + H_2$ or other species. Nevertheless, we decided to examine whether overlap of the a_1 Rydberg-like orbitals on two neighboring NH_4 units would provide a strong enough attraction to stabilize $(NH_4)_2$ sufficiently to render it stable to fragmentation into 2 NH_4.. The energy required to effect the transition from $(NH_4)_2$ to 2 NH_4, with the bond lengths and angles held at the respective equilibrium values for $(NH_4)_2$ and NH_4, we define as the strength of the two-electron Rydberg bond in this case.

As noted above, neutral NH_4 is isoelectronic with the Na atom, so its lowest-energy occupied a_1 molecular orbital, which is vacant in the NH_4^+ cation but singly occupied in neutral NH_4, could be expected to play a role analogous to the 3s orbital of Na but there will be differences because Na and NH_4 do not have equivalent electronegativites. The electron binding energy of the NH_4 orbital (4 eV[8]) is lower than that of 3s Na (5.1 eV[8]), and the vertical electron affinity of NH_4 (0.42 eV[8]) is smaller than that of Na (0.72 eV[8]), so the Mulliken electronegativity of Na is expected to be approximately $5.82/4.42 = 1.3$ times that of NH_4. Hence, the bonding in the $(NH_4)Na$ species studied here is expected to be covalent and polar but not ionic. The $(NH_4)Li$ and $(NH_4)K$ molecules, likewise, should each possess a polar but covalent Rydberg-valence bond because the electronegativities of Li and K are not much different from that of Na.

It is known that Na_2 forms a reasonably strong (ca. 17 kcal/mol[9]) covalent bond and that the molecular cation Na_2^+ is even more stable with respect to fragmentation into $Na + Na^+$. Indeed, in our earlier study, we found that the $(NH_4)_2$ Rydberg dimer, which has N−H bond lengths very near those of NH_4^+ and nearly tetrahedral internal angles, is stable with respect to dissociation into 2 NH_4 with a dissociation energy of $D_0 \approx 9$ kcal/mol. This particular Rydberg bond thus has an energy comparable to hydrogen bonds or van der Waals attractions but is substantially weaker than normal chemical bonds involving valence orbitals. In that earlier study, we also noted that the one-electron Rydberg bond in $(NH_4)_2^+$ is even stronger ($D_0 \approx$ 20 kcal/mol[1,10,11]) than for the neutral, analogous to the Na_2/Na_2^+ case.

Although the $(NH_4)_2$ dimer is stable with respect to dissociation into the two Rydberg radicals, Wright and McKay[12] observed that it is highly thermodynamically unstable[13] with respect to dissociation into 2 $NH_3 + H_2$ and the barrier connecting the locally stable $(NH_4)_2$ to these products is too small to render the Rydberg-bound dimer long-lived. That is, as shown in ref 12, the geometrically and electronically stable $(NH_4)_2$ local minimum is separated from the $2NH_3 + H_2$ products by a very small barrier (1.8−2.4 kcal/mol), and, when zero-point energy corrections (ZPE) are taken into account, $(NH_4)_2$ lies above (by about 5 kcal/mol) this barrier. As a result, Wright and McKay[12] concluded that the lifetime of the $(NH_4)_2$ Rydberg dimer would be of the order of 1 ns as a result of which its experimental observation would be very difficult. We repeated the study of Wright and McKay at the MP2(full)/6-31++G** level (which was used in our previous calculations[1] on $(NH_4)_2$) and found a barrier to dissociation of 3.43 kcal/mol. After considering ZPE corrections, we found $(NH_4)_2$ to lie 3.2 kcal/mol above this barrier, similar to what was found in ref 12. Even when H is replaced by D or T to form $(ND_4)_2$ or $(NT_4)_2$, the barrier to dissociation is not large enough to cause the neutral dimer, with its ZPE, to lie below the barrier.

Although we have continued to search for alternative candidates (e.g., $(H_3O)_2$, H_3ONH_4 and others[14]) that might form stronger two-electron Rydberg−Rydberg bonds with higher barriers, we have not yet found a satisfactorily convincing candidate. However, it is important to keep in mind, as noted earlier, that the corresponding one-electron Rydberg−Rydberg bound cations are predicted to be stable with respect to

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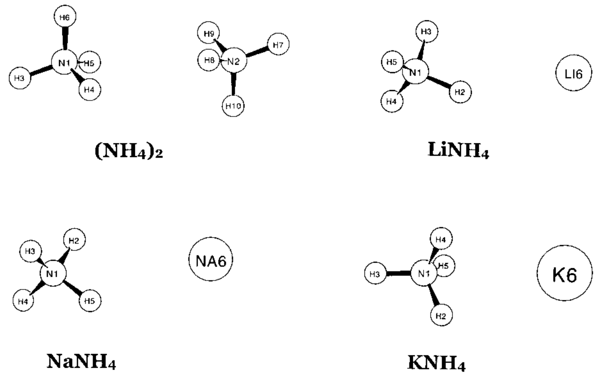
TABLE 1: Calculated Molecular Properties of the Minimum-Energy $LiNH_4$ Structure

$LiNH_4$ (C_{3v}, $^1A_1$)[a]	$LiNH_4$ (C_s, $^1A'$)	$LiNH_4$ (C_s, $^1A'$)[b]
$1a_1^2 2a_1^2 1e^4 3a_1^2$	$1a'^2 1a''^2 2a'^2 3a'^2 4a'^2$	$1a'^2 1a''^2 2a'^2 3a'^2 4a'^2$
SCF/6-311++G**	MP2(full)/6-311++G**	CCSD(T)/6-311++G**
$E_{SCF} = -64.138779$ au	$E_{MP2} = -64.399687$ au	$E_{CCSD(T)} = -64.397560$ au
$\angle R_e(N-H_2) = 1.044$ Å	$R_e(N-H_2) = 1.088$ Å	$R_e(N-H_2) = 1.070$ Å
$\angle R_e(N-H_{3,4,5}) = 1.012$ Å	$R_e(N-H_3) = 1.030$ Å	$R_e(N-H_3) = 1.035$ Å
$\angle R_e(Li-H_2) = 2.589$ Å	$R_e(N-H_{4,5}) = 1.030$ Å	$R_e(N-H_{4,5}) = 1.034$ Å
$\angle H_2NH_{3,4,5} = 108.3°$	$R_e(Li-H_2) = 2.346$ Å	$R_e(Li-H_2) = 2.470$ Å
$\angle H_3NH_{4,5} = 110.6°$	$\angle H_2NH_3 = 107.1°$	$\angle H_2NH_3 = 105.0°$
$\angle LiNH_2 = 180.0°$	$\angle H_2NH_{4,5} = 109.4°$	$\angle H_2NH_{4,5} = 107.2°$
	$\angle H_3NH_{4,5} = 110.0°$	$\angle H_3NH_{4,5} = 110.0°$
	$\angle H_4NH_5 = 110.8°$	$\angle H_4NH_5 = 111.3°$
	$\angle LiNH_2 = 165.4°$	$\angle LiNH_2 = 141.4°$
$\omega_1(a_1) = 3524$ cm^{-1}	$\omega_1(a') = 3426$ cm^{-1}	$\omega_1(a') = 3332$ (2459) cm^{-1}
$\omega_2(a_1) = 2926$ cm^{-1}	$\omega_2(a') = 3251$ cm^{-1}	$\omega_2(a') = 3199$ (2286) cm^{-1}
$\omega_3(a_1) = 1484$ cm^{-1}	$\omega_3(a') = 2196$ cm^{-1}	$\omega_3(a') = 2573$ (1889) cm^{-1}
$\omega_4(a_1) = 230$ cm^{-1}	$\omega_4(a') = 1605$ cm^{-1}	$\omega_4(a') = 1604$ (1138) cm^{-1}
$\omega_5(e) = 3661$ cm^{-1}	$\omega_5(a') = 1358$ cm^{-1}	$\omega_5(a') = 1377$ (1031) cm^{-1}
$\omega_6(e) = 1797$ cm^{-1}	$\omega_6(a') = 1304$ cm^{-1}	$\omega_6(a') = 1318$ (982) cm^{-1}
$\omega_7(e) = 1543$ cm^{-1}	$\omega_7(a') = 262$ cm^{-1}	$\omega_7(a') = 248$ (236) cm^{-1}
$\omega_8(e) = 115$ cm^{-1}	$\omega_8(a') = 110$ cm^{-1}	$\omega_8(a') = 67$ (50) cm^{-1}
	$\omega_9(a'') = 3428$ cm^{-1}	$\omega_9(a'') = 3369$ (2428) cm^{-1}
	$\omega_{10}(a'') = 1608$ cm^{-1}	$\omega_{10}(a'') = 1614$ (1146) cm^{-1}
	$\omega_{11}(a'') = 1338$ cm^{-1}	$\omega_{11}(a'') = 1380$ (1028) cm^{-1}
	$\omega_{12}(a'') = 85$ cm^{-1}	$\omega_{12}(a'') = 94$ (67) cm^{-1}
ZPE = 32.02 kcal/mol	ZPE = 28.55 kcal/mol	ZPE = 28.84 (21.16) kcal/mol

[a] Li is coordinated to the vertex of the NH_4 group in the most stable structure of $LiNH_4$ at the SCF/6-311++G** level of theory. The structure with Li coordinated to the face of the NH_4 group is a local minimum too, but it is somewhat higher in energy. However, both of those structures are second-order saddle points at the MP2(full)/6-311+G** level of theory. The structure with Li coordinated to the edge of the NH_4 group is a second-order saddle point at the SCF/6-311+G* level of theory, and it is a first-order saddle point at the MP2(FULL)/6-311++G** level of theory. [b] Data in parentheses are for the $LiND_4$ isotopomer.



$(NH_4)_2$ **$LiNH_4$**

$NaNH_4$ **KNH_4**

Figure 1. Minimum-energy structures of $(NH_4)_2$, $(NH_4)Li$, $(NH_4)Na$ at the CCSD(T)/6-311++G** level, and of $(NH_4)K$ at the MP2(FULL)/Gen level.

dissociation and thus likely represent better candidates for experimental observation. Certainly, the ultimate solution to finding better candidates in the neutral-molecule case would be to find a system with a strong Rydberg bond whose various fragmentation products do not involve extremely strong bonds. In this manner, one might be able to find a thermodynamically stable Rydberg-bound molecule. Unfortunately, thus far we have not been able to find such a species.

In the present work, we explore the possibility that *mixed Rydberg-valence bonding* interactions might produce species of sufficient stability to be observed in the laboratory. Specifically, we decided to examine bonding between NH_4 (with its Rydberg-like a_1 orbital singly occupied) and the alkali atoms Li, Na, and K (which have their 2s, 3s, or 4s valence orbital singly occupied). In each of the resultant Rydberg-valence bound species (i.e., $(NH_4)Li$, $(NH_4)Na$, and $(NH_4)K$), the stability of the complex with respect to dissociation into NH_4 and an alkali atom as well as dissociation into NH_3 and the corresponding alkali hydride must be determined. The latter dissociation pathway is expected to be the most problematic with respect to the stability of the Rydberg-valence bound molecule because the bonds in the alkali hydrides are quite strong (2.43 eV for LiH,[9] 1.91 eV for NaH,[9] and 1.77 eV for KH[9]).

II. Computational Methods

We first optimized the local-minimum geometries of the NH_4-Li and NH_4Na complexes employing analytical gradients with polarized split-valence basis sets (6-311++G**[15−17]) at the SCF and MP2 (full) (meaning all electrons were included in the correlation calculations) levels.[18] These geometries were than refined using the CCSD(T)/6-311++G** level of theory.[19−21] In all cases, we identified geometries at which the Rydberg-valence bound species were locally geometrically stable (i.e., where all of the local harmonic vibrational frequencies were real). The local minimum and transition state geometries of the NH_4K complex were optimized at the SCF and MP2(full) levels of theory using (14s6p/9s6p)[22] basis sets expanded by one d (α = 0.95 optimized for KH), one diffuse s (α = 0.006), and two diffuse p (α = 0.08 and α = 0.027) functions for K (giving a final contraction that can be denoted (5,1,2,1,1,1,1,1,1,1/5,1,1,1,1,1/1)) and the standard 6-311++G** basis sets for N and H (we label this basis "Gen" in this article). For the K-containing compounds, one cannot ignore core-valence correlations;[23,24] therefore, CCSD(T) calculations without the core electrons included are not expected to be accurate, so such calculations were not performed. However, CCSD(T,FULL) calculations with all electrons included are very computer-time intensive; therefore, only single-point calculations were performed at this level of theory for NH_4K.

A similar strategy was used to locate the *transition-state* geometries and associated energy barriers along the fragmentation paths leading from the Rydberg-valence bound molecules to NH_3 plus the alkali hydride products. The paths leading from the Rydberg-valence bound species to NH_4 plus an alkali atom

TABLE 2: Calculated Molecular Properties of the $LiNH_4$ Transition State Structure[a]

$LiNH_4$ (C_{3v}, $^1A_1$)	$LiNH_4$ (C_{3v}, $^1A_1$)	$LiNH_4$ (C_{3v}, $^1A_1$)
$1a_1^2 1e^4 2a_1^2 3a_1^2$	$1a_1^2 1e^4 2a_1^2 3a_1^2$	$1a_1^2 1e^4 2a_1^2 3a_1^2$
SCF/6-311++G**	MP2(full)/6-311++G**	CCSD(T)/6-311++G**
$E_{SCF} = -64.123405$ au	$E_{MP2} = -64.396429$ au	$E_{CCSD(T)} = -64.393026$ au
$R_e(N-H_2) = 1.389$ Å	$R_e(N-H_2) = 1.313$ Å	$R_e(N-H_2) = 1.323$ Å
$R_e(N-H_{3,4,5}) = 1.007$ Å	$R_e(N-H_{3,4,5}) = 1.025$ Å	$R_e(N-H_{3,4,5}) = 1.026$ Å
$R_e(Li-H_2) = 2.063$ Å	$R_e(Li-H_2) = 2.034$ Å	$R_e(Li-H_2) = 2.042$ Å
$\angle H_2NH_{3,4,5} = 108.8°$	$\angle H_2NH_{3,4,5} = 109.5°$	$\angle H_2NH_{3,4,5} = 109.7°$
$\angle H_3NH_{4,5} = 110.1°$	$\angle H_3NH_{4,5} = 109.4°$	$\angle H_3NH_{4,5} = 109.2°$
$\angle LiNH_2 = 180.0°$	$\angle LiNH_2 = 180.0°$	$\angle LiNH_2 = 180.0°$
$\omega_1(a_1) = 3594$ cm^{-1}	$\omega_1(a_1) = 3325$ cm^{-1}	$\omega_1(a_1) = 3322$ (2366) cm^{-1}
$\omega_2(a_1) = 1246$ cm^{-1}	$\omega_2(a_1) = 1200$ cm^{-1}	$\omega_2(a_1) = 1218$ (930) cm^{-1}
$\omega_3(a_1) = 354$ cm^{-1}	$\omega_3(a_1) = 347$ cm^{-1}	$\omega_3(a_1) = 338$ (329) cm^{-1}
$\omega_4(a_1) = 1866$ i cm^{-1}	$\omega_4(a_1) = 1352$ i cm^{-1}	$\omega_4(a_1) = 1436$ i (1035 i) cm^{-1}
$\omega_5(e) = 3772$ cm^{-1}	$\omega_5(e) = 3533$ cm^{-1}	$\omega_5(e) = 3512$ (2592) cm^{-1}
$\omega_6(e) = 1756$ cm^{-1}	$\omega_6(e) = 1589$ cm^{-1}	$\omega_6(e) = 1588$ (1151) cm^{-1}
$\omega_7(e) = 963$ cm^{-1}	$\omega_7(e) = 949$ cm^{-1}	$\omega_7(e) = 924$ (673) cm^{-1}
$\omega_8(e) = 280$ cm^{-1}	$\omega_8(e) = 200$ cm^{-1}	$\omega_8(e) = 166$ (121) cm^{-1}
ZPE = 26.78 kcal/mol	ZPE = 24.89 kcal/mol	ZPE = 24.67 (18.15) kcal/mol
$h_{SCF} = 9.65$ kcal/mol	$h_{MP2} = 2.04$ kcal/mol	$h_{CCSD(T)} = 2.85$ kcal/mol
$h_{SCF+ZPE} = 4.42$ kcal/mol	$h_{MP2+ZPE} = -1.62$ kcal/mol	$h_{CCSD(T)+ZPE} = -1.32$ (-0.16) kcal/mol

[a] Data in parentheses are for the $LiND_4$ isotopomer.

TABLE 3: Calculated Molecular Properties of the Minimum-Energy $NaNH_4$ Structure

$NaNH_4$ (C_{3v}, $^1A_1$)[a]	$NaNH_4$ (C_{3v}, $^1A_1$)	$NaNH_4$ (C_{3v}, $^1A_1$)
$1a_1^2 2a_1^2 1e^4 3a_1^2$	$1a^2 2a^2 3a^2 4a^2 5a^2$	$1a^2 2a^2 3a^2 4a^2 5a^2$
SCF/6-311++G**	MP2(full)/6-311++G**	CCSD(T)/6-311++G**
$E_{SCF} = -218.550367$ au	$E_{MP2} = -218.928910$ au	$E_{CCSD(T)} = -218.807012$ au
$R_e(N-H_2) = 1.017$ Å	$R_e(N-H_2) = 1.045$ Å	$R_e(N-H_2) = 1.048$ Å
$R_e(N-H_{3,4,5}) = 1.018$ Å	$R_e(N-H_3) = 1.036$ Å	$R_e(N-H_3) = 1.037$ Å
$R_e(Na-H_{3,4,5}) = 3.400$ Å	$R_e(N-H_4) = 1.033$ Å	$R_e(N-H_4) = 1.037$ Å
$R_e(Na-N) = 3.645$ Å	$R_e(N-H_5) = 1.046$ Å	$R_e(N-H_5) = 1.047$ Å
$\angle H_2NH_{3,4,5} = 111.8°$	$R_e(Na-H_2) = 2.948$ Å	$R_e(Na-H_2) = 2.991$ Å
$\angle H_3NH_{4,5} = 107.0°$	$R_e(Na-H_5) = 2.947$ Å	$R_e(Na-H_5) = 2.992$ Å
	$\angle H_2NH_3 = 111.2°$	$\angle H_2NH_3 = 110.0°$
	$\angle H_2NH_4 = 108.8°$	$\angle H_2NH_4 = 109.8°$
	$\angle H_2NH_5 = 104.7°$	$\angle H_2NH_5 = 105.3°$
	$\angle H_3NH_4 = 111.8°$	$\angle H_3NH_4 = 111.3°$
	$\angle H_3NH_5 = 111.2°$	$\angle H_3NH_5 = 110.4°$
	$\angle H_4NH_5 = 108.8°$	$\angle H_4NH_5 = 109.9°$
	$\angle NaNH_2 = 109.7°$	$\angle NaNH_2 = 111.2°$
$\omega_1(a_1) = 3584$ cm^{-1}	$\omega_1 = 3358$ cm^{-1}	$\omega_1 = 3311$ (2446) cm^{-1}
$\omega_2(a_1) = 3417$ cm^{-1}	$\omega_2 = 3257$ cm^{-1}	$\omega_2 = 3221$ (2360) cm^{-1}
$\omega_3(a_1) = 1561$ cm^{-1}	$\omega_3 = 3034$ cm^{-1}	$\omega_3 = 3020$ (2216) cm^{-1}
$\omega_4(a_1) = 137$ cm^{-1}	$\omega_4 = 3026$ cm^{-1}	$\omega_4 = 2994$ (2152) cm^{-1}
$\omega_5(e) = 3508$ cm^{-1}	$\omega_5 = 1620$ cm^{-1}	$\omega_5 = 1614$ (1142) cm^{-1}
$\omega_6(e) = 1797$ cm^{-1}	$\omega_6 = 1607$ cm^{-1}	$\omega_6 = 1603$ (1134) cm^{-1}
$\omega_7(e) = 1520$ cm^{-1}	$\omega_7 = 1390$ cm^{-1}	$\omega_7 = 1386$ (1036) cm^{-1}
$\omega_8(e) = 91$ cm^{-1}	$\omega_8 = 1372$ cm^{-1}	$\omega_8 = 1376$ (1031) cm^{-1}
	$\omega_9 = 1327$ cm^{-1}	$\omega_9 = 1334$ (997) cm^{-1}
	$\omega_{10} = 152$ cm^{-1}	$\omega_{10} = 141$ (133) cm^{-1}
	$\omega_{11} = 78$ cm^{-1}	$\omega_{11} = 120$ (85) cm^{-1}
	$\omega_{12} = 27$ cm^{-1}	$\omega_{12} = 65$ (46) cm^{-1}
ZPE = 32.21 kcal/mol	ZPE = 28.95 kcal/mol	ZPE = 28.85 (21.13) kcal/mol

[a] Na is coordinated to the face of the NH_4 group in the most stable structure of $NaNH_4$ at the SCF/6-311++G** level of theory. The structure with Na coordinated to the vertex of the NH_4 group is a local minimum too, but it is somewhat higher in energy. However, both of those structures are second-order saddle points at the MP2(FULL)/6-311+G** level of theory. The structure with Na coordinated to the edge of the NH_4 group is a first-order saddle point at the both SCF/6-311++G** and MP2(FULL)/6-311++G** levels of theory. [b] Data in parentheses are for the $NaND_4$ isotopomer.

have no barriers above their reaction endothermicity. The harmonic vibrational frequencies at the CCSD(T)/6-311++G** level of theory were calculated numerically. Single-point energy calculations at the CCSD(T)/6-311++G(2df,2pd) level of theory for NH_4Li, NH_4Na and at the CCSD(T,FULL)/Gen level of theory for NH_4K were carried out at the local-minimum and at the barrier geometries obtained at the CCSD(T)/6-311++G** (NH_4Li and NH_4Na) level and MP2(FULL)/Gen (NH_4K) level, respectively. The fundamental vibrational frequencies, vibrational normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods, and all of these calculations were carried out with the Gaussian 94 program.[25]

III. Results and Discussion

In Tables 1, 3, and 5, we present our SCF, MP2, and CCSD(T) level findings (geometries, local harmonic frequencies) on the minimum-energy structures of $(NH_4)Li$, $(NH_4)Na$, and $(NH_4)K$, respectively. In Tables 2, 4, and 6, analogous information is given for the transition-state structures that connect to the NH_3 plus alkali hydride products. It is our feeling that

TABLE 4: Calculated Molecular Properties of the NaNH$_4$ Transition State Structure[a]

NaNH$_4$ (C_{3v}, ^{1}A$_1$)	NaNH$_4$ (C_{3v}, ^{1}A$_1$)	NaNH$_4$ (C_{3v}, ^{1}A$_1$)
$1a_1^2 1e^4 2a_1^2 3a_1^2$	$1a_1^2 1e^4 2a_1^2 3a_1^2$	$1a_1^2 1e^4 2a_1^2 3a_1^2$
SCF/6-311++G**	MP2(full)/6-311++G**	CCSD(T)/6-311++G**
$E_{\mathrm{SCF}} = -218.527755$ au	$E_{\mathrm{MP2}} = -218.920875$ au	$E_{\mathrm{CCSD(T)}} = -218.797710$ au
$R_e(\mathrm{N-H_2}) = 1.453$ Å	$R_e(\mathrm{N-H_2}) = 1.391$ Å	$R_e(\mathrm{N-H_2}) = 1.377$ Å
$R_e(\mathrm{N-H_{3,4,5}}) = 1.005$ Å	$R_e(\mathrm{N-H_{3,4,5}}) = 1.024$ Å	$R_e(\mathrm{N-H_{3,4,5}}) = 1.025$ Å
$R_e(\mathrm{Na-H_2}) = 2.268$ Å	$R_e(\mathrm{Na-H_2}) = 2.215$ Å	$R_e(\mathrm{Na-H_2}) = 2.276$ Å
$\angle \mathrm{H_2NH_{3,4,5}} = 108.8°$	$\angle \mathrm{H_2NH_{3,4,5}} = 109.7°$	$\angle \mathrm{H_2NH_{3,4,5}} = 109.9°$
$\angle \mathrm{H_3NH_{4,5}} = 110.1°$	$\angle \mathrm{H_3NH_{4,5}} = 109.3°$	$\angle \mathrm{H_3NH_{4,5}} = 109.0°$
$\angle \mathrm{NaNH_2} = 180.0°$	$\angle \mathrm{NaNH_2} = 180.0°$	$\angle \mathrm{NaNH_2} = 180.0°$
$\omega_1(a_1) = 3602$ cm^{-1}	$\omega_1(a_1) = 3342$ cm^{-1}	$\omega_1(a_1) = 3328$ (2370) cm^{-1}
$\omega_2(a_1) = 1210$ cm^{-1}	$\omega_2(a_1) = 1163$ cm^{-1}	$\omega_2(a_1) = 1194$ (910) cm^{-1}
$\omega_3(a_1) = 252$ cm^{-1}	$\omega_3(a_1) = 244$ cm^{-1}	$\omega_3(a_1) = 222$ (210) cm^{-1}
$\omega_4(a_1) = 1756$ i cm^{-1}	$\omega_4(a_1) = 1269$ i cm^{-1}	$\omega_4(a_1) = 1434$ i (1037 i) cm^{-1}
$\omega_5(e) = 3781$ cm^{-1}	$\omega_5(e) = 3551$ cm^{-1}	$\omega_5(e) = 3518$ (2597) cm^{-1}
$\omega_6(e) = 1757$ cm^{-1}	$\omega_6(e) = 1588$ cm^{-1}	$\omega_6(e) = 1588$ (1151) cm^{-1}
$\omega_7(e) = 840$ cm^{-1}	$\omega_7(e) = 808$ cm^{-1}	$\omega_7(e) = 806$ (587) cm^{-1}
$\omega_8(e) = 238$ cm^{-1}	$\omega_8(e) = 175$ cm^{-1}	$\omega_8(e) = 133$ (95) cm^{-1}
ZPE = 26.17 kcal/mol	ZPE = 24.29 kcal/mol	ZPE = 24.07 (17.66) kcal/mol
$h_{\mathrm{SCF}} = 14.19$ kcal/mol	$h_{\mathrm{MP2}} = 5.04$ kcal/mol	$h_{\mathrm{CCSD(T)}} = 5.84$ kcal/mol
$h_{\mathrm{SCF+ZPE}} = 8.15$ kcal/mol	$h_{\mathrm{MP2+ZPE}} = 0.38$ kcal/mol	$h_{\mathrm{CCSD(T)+ZPE}} = 1.05$ (2.37) kcal/mol

[a] Data in parentheses are for the NaND$_4$ isotopomer.

TABLE 5: Calculated Molecular Properties of the Minimum-Energy KNH$_4$ Structure

KNH$_4$ (C_{3v}, ^{1}A$_1$)[a]	KNH$_4$ (C_{3v}, ^{1}A$_1$)[a,b]	KNH$_4$ (C_{3v}, ^{1}A$_1$)
$1a_1^2 2a_1^2 1e^4 3a_1^2$	$1a_1^2 2a_1^2 1e^4 3a_1^2$	$1a_1^2 2a_1^2 1e^4 3a_1^2$
SCF/Gen	MP2(full)/Gen	CCSD(T,FULL)/Gen
$E_{\mathrm{SCF}} = -655.854889$ au	$E_{\mathrm{MP2}} = -656.379316$ au	$E_{\mathrm{CCSD(T)}} = -656.418842$ au
$R_e(\mathrm{N-H_3}) = 1.017$ Å	$R_e(\mathrm{N-H_{2,4,5}}) = 1.042$ Å	
$R_e(\mathrm{N-H_{2,4,5}}) = 1.019$ Å	$R_e(\mathrm{N-H_3}) = 1.040$ Å	
$R_e(\mathrm{K-H_{2,4,5}}) = 3.869$ Å	$R_e(\mathrm{K-H_{2,4,5}}) = 3.533$ Å	
$R_e(\mathrm{K-N}) = 4.121$ Å	$R_e(\mathrm{K-N}) = 3.780$ Å	
$\angle \mathrm{H_{2,4,5}NH_3} = 111.3°$	$\angle \mathrm{H_{2,4,5}NH_3} = 111.5°$	
$\angle \mathrm{H_2NH_{4,5}} = 107.6°$	$\angle \mathrm{H_2NH_{3,4}} = 107.4°$	
$\omega_1(a_1) = 3564$ cm^{-1}	$\omega_1(a_1) = 3239$ (2392) cm^{-1}	
$\omega_2(a_1) = 3397$ cm^{-1}	$\omega_2(a_1) = 3053$ (2160) cm^{-1}	
$\omega_3(a_1) = 1550$ cm^{-1}	$\omega_3(a_1) = 1384$ (1035) cm^{-1}	
$\omega_4(a_1) = 106$ cm^{-1}	$\omega_4(a_1) = 114$ (107) cm^{-1}	
$\omega_5(e) = 3487$ cm^{-1}	$\omega_5(e) = 3146$ (2326) cm^{-1}	
$\omega_6(e) = 1796$ cm^{-1}	$\omega_6(e) = 1588$ (1124) cm^{-1}	
$\omega_7(e) = 1516$ cm^{-1}	$\omega_7(e) = 1343$ (1004) cm^{-1}	
$\omega_8(e) = 103$ cm^{-1}	$\omega_8(e) = 41$ (29) cm^{-1}	
ZPE = 32.05 kcal/mol	ZPE = 28.63 (20.96) kcal/mol	

[a] K is coordinated to the face of the NH$_4$ group in the most stable structure of KNH$_4$ at the SCF/Gen and MP2(FULL)/Gen levels of theory. The structure with K coordinated to the vertex of the NH$_4$ group is a second-order saddle point at both levels of theory. The structure with K coordinated to the edge of the NH$_4$ group is a first-order saddle point at both SCF/Gen and MP2(FULL)/Gen levels of theory. [b] Data in parentheses are for the KND$_4$ isotopomer.

providing data at various levels of theory is important in this case because (a) these are new species that have not yet been experimentally confirmed so it is important to offer considerable detail to characterize them, and (b) because the local-minimum to transition state energy differences are small enough to make it important to demonstrate that the findings are not likely artifacts of the particular methods used. One can see that geometries and even symmetries of the minima structures are quite different at the SCF level of theory compare to those at the MP2(FULL) and CCSD(T) level of theories, while they are very close at the MP2(FULL) and CCSD(T) level of theories.

A. Equilibrium Structures. Figure 1 shows the equilibrium structures of all three species in a manner that makes it clear their nuclear frameworks consist of an essentially intact (NH$_4^+$) moiety and an alkali atom. Further structural details are given in Tables 1, 2, and 5 where one can note that the N−H bond lengths and vibrational frequencies are close to those in NH$_4^+$ (of course, there are also three low-frequency vibrations in the complexes that do not occur in NH$_4^+$). The minimum-energy geometries of the three species do not all possess the same symmetries (i.e., the alkali atom seems to be coordinated most closely to 1, 2, or 3 N−H bonds in the three different structures), although the two low-frequency “bending” modes, which cause the NH$_4^+$ group to rotate about the alkali-N interatomic axis, are so soft as to render the energy differences associated with these internal geometry differences very small.

The fact that all vibrational frequencies given in Tables 1, 3, and 5 are real shows that the (NH$_4$)M (M = Li, Na, K) species are indeed local minima on their respective energy surfaces. The observation that all N−H bond lengths are nearly identical (ca. 1.03−1.05 Å and are close to the bond length in NH$_4^+$ supports our picture of bonding between an alkali atom and an intact Rydberg (NH$_4$) molecule.

B. Thermochemistry and Bond Strengths. In Table 7 are summarized our CCSD(T) level findings for the Rydberg-valence bond strengths for (NH$_4$)Li, (NH$_4$)Na, and (NH$_4$)K dissociating into NH$_4$ plus an alkali atom as well as the energy released when the complex fragments into NH$_3$ + LiH/NaH/KH. The predicted strengths of the Rydberg-valence bonds range from 9 to 16 kcal/mol, which are similar to what we obtained for the (NH$_4$)$_2$ case (9.1 kcal/mol). In contrast to the (NH$_4$)$_2$ case, the energy release when the (NH$_4$)M dissociates to NH$_3$

TABLE 6: Calculated Molecular Properties of the KNH_4 Transition State Structure[a]

KNH_4 (C_{3v}, $^1A_1$)	KNH_4 (C_{3v}, $^1A_1$)	KNH_4 (C_{3v}, $^1A_1$)
$1a_1^2 1e^4 2a_1^2 3a_1^2$	$1a_1^2 1e^4 2a_1^2 3a_1^2$	$1a_1^2 1e^4 2a_1^2 3a_1^2$
SCF/Gen	MP2(full)/Gen	CCSD(T,FULL)/Gen
$E_{SCF} = -655.824499$ au	$E_{MP2} = -656.364367$ au	$E_{CCSD(T,FULL)} = -656.404439$ au
$R_e(N-H_2) = 1.493$ Å	$R_e(N-H_2) = 1.465$ Å	
$R_e(N-H_{3,4,5}) = 1.006$ Å	$R_e(N-H_{3,4,5}) = 1.025$ Å	
$R_e(K-H_2) = 2.748$ Å	$R_e(K-H_2) = 2.612$ Å	
$\angle H_2NH_{3,4,5} = 108.7°$	$\angle H_2NH_{3,4,5} = 110.0°$	
$\angle H_3NH_{4,5} = 110.2°$	$\angle H_3NH_{4,5} = 109.0°$	
$\angle KNH_2 = 180.0°$	$\angle KNH_2 = 180.0°$	
$\omega_1(a_1) = 3587$ cm^{-1}	$\omega_1(a_1) = 3327$ (2369) cm^{-1}	
$\omega_2(a_1) = 1185$ cm^{-1}	$\omega_2(a_1) = 1137$ (865) cm^{-1}	
$\omega_3(a_1) = 179$ cm^{-1}	$\omega_3(a_1) = 187$ (175) cm^{-1}	
$\omega_4(a_1) = 1780$ i cm^{-1}	$\omega_4(a_1) = 1137$ i (825 i) cm^{-1}	
$\omega_5(e) = 3773$ cm^{-1}	$\omega_5(e) = 3544$ (2616) cm^{-1}	
$\omega_6(e) = 1753$ cm^{-1}	$\omega_6(e) = 1580$ (1146) cm^{-1}	
$\omega_7(e) = 740$ cm^{-1}	$\omega_7(e) = 665$ (485) cm^{-1}	
$\omega_8(e) = 233$ cm^{-1}	$\omega_8(e) = 111$ (79) cm^{-1}	
ZPE = 25.66 kcal/mol	ZPE = 23.52 (17.24) kcal/mol	
$h_{SCF} = 19.07$ kcal/mol	$h_{MP2} = 9.38$ kcal/mol	$h_{CCSD(T,FULL)} = 9.04$ kcal/mol
$h_{SCF+ZPE} = 12.68$ kcal/mol	$h_{MP2+ZPE} = 4.27$ (5.67) kcal/mol	$h_{CCSD(T,FULL)+ZPE} = 3.93$ (5.32) kcal/mol

[a] Data in parentheses are for the KND_4 isotopomer.

TABLE 7: Calculated Dissociation Energies and Dissociation Barriers of $LiNH_4$, $NaNH_4$, and KNH_4

reaction	ΔE (kcal/mol)	ΔE+ZPE (kcal/mol)
$LiNH_4 \rightarrow$ TS	2.85[a]	−1.32[a]
$LiNH_4 \rightarrow Li + NH_4$	+16.71[a]	+15.86[a,b]
$LiNH_4 \rightarrow LiH + NH_3$	−37.09[a]	−42.27[a,b]
$NaNH_4 \rightarrow$ TS	5.84[a]	1.05[a]
$NaNH_4 \rightarrow Na + NH_4$	+13.74[a]	+12.88[a,b]
$NaNH_4 \rightarrow NaH + NH_3$	−27.79[a]	−33.35[a,b]
$KNH_4 \rightarrow$ TS	+9.04[c]	+3.93[c,d]
$KNH_4 \rightarrow K + NH_4$	+9.86[c]	+9.23[c,d]
$KNH_4 \rightarrow KH + NH_3$	−18.99[c]	−24.65[c,d]

[a] At the CCSD(T)/6-311++G(2df,2pd)/CCSD(T)/6-311++G** level of theory. [b] ZPE at the CCSD(T)/6-311++G** level of theory. [c] At the CCSD(T,FULL)/Gen/MP2(FULL)/Gen level of theory. [d] ZPE at the MP2(FULL)/Gen level of theory.

plus an alkali hydride is considerably smaller (ranging from 24 to 42 kcal/mol) than when $(NH_4)_2$ dissociates into $NH_3 + H_2$ (87 kcal/mol), as we expected. The reduced exothermicity of the lowest-energy dissociation path compared to the $(NH_4)_2$ case suggests that the $(NH_4)M$ species should have higher barriers to this dissociation and thus increased stability, which indeed is born out as we expected.

C. Barriers to Fragmentation and Stability of Rydberg-valence Bound Species. As Table 7 also shows, the barriers to dissociation into NH_3 + MH in our Rydberg-valence species are comparable to or higher than the 2−3 kcal/mol (without zero-point energy correction) found for $(NH_4)_2$, but are still quite small. The largest barrier occurs for $(NH_4)K$ and is only 9.04 kcal/mol; those for the Li and Na complexes are 2.85 and 5.84 kcal/mol, respectively. However, when zero-point energies are included, the total energy of $Li(NH_4)$ at its equilibrium geometry is predicted to lie above the energy of the corresponding transition state. In contrast, $Na(NH_4)$, $Na(ND_4)$, $K(NH_4)$ and $K(ND_4)$ are predicted to lie below their transition states by 1.05, 2.37, 3.93 and 5.32 kcal/mol, respectively.

D. Nature of the Rydberg-Valence Bonding Molecular Orbital. In Figure 2, we show contour representations of the Rydberg-valence bonding orbital[26] for the $(NH_4)_2$ that we examined in our earlier work as well as for $(NH_4)Li$, $(NH_4)Na$, and $(NH_4)K$. These orbitals clearly display (a) large density in the region between the two fragment moieties as well as (b) nodal surfaces and secondary densities that reflect that requirement that this bonding orbital be orthogonal to all of the occupied valence orbitals of the (NH_4) and alkali atoms. The covalent yet not highly polar nature of the bonding causes these orbitals to not be strongly spatially polarized toward the (NH_4) or toward the alkali species. The energies required to remove an electron from one of these bonding Rydberg-valence orbitals, as computed using the outer valence Green function method,[27−31] are 3.7, 4.5, 4.4, and 3.9 eV (all using 6-311++G(2df,2pd) basis sets, except $(NH_4)K$, where Gen basis sets were used), respectively, for $(NH_4)_2$, $(NH_4)Li$, $(NH_4)Na$, and $(NH_4)K$.

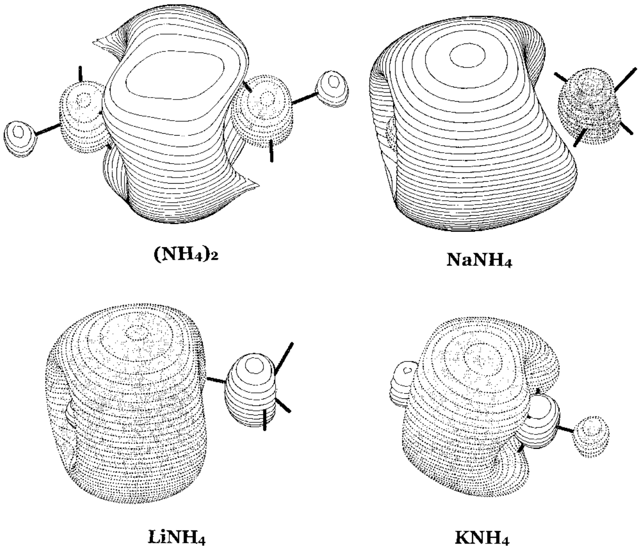


Figure 2. Highest occupied molecular orbitals in $(NH_4)_2$, $(NH_4)Li$, $(NH_4)Na$, and $(NH_4)K$.

IV. Summary

The bonding between (NH_4) and three alkali atoms (Li, Na, and K) has been examined using ab initio methods that include flexible and diffuse atomic orbital basis sets and that treat electron correlation. Our findings suggest that $(NH_4)Na$ and $(NH_4)K$ may be energetically stable enough (i.e., to have large enough barriers to fragmentation to (NH_4) plus the alkali hydride) to be detected experimentally if they can be formed, but $(NH_4)Li$ has such a small barrier that it likely will be impossible or much more difficult to observe. Because, as calculations we have performed and plan to report in a forthcoming paper indicate, the corresponding cations ($(NH_4)Na^+$ and $(NH_4)K^+$) are much more stable with repect to fragmentation than these neutrals, it is much more likely that the cations can be experimetally probed. If such experiments were successful, it may be possible, albeit difficult, to form the neutral Rydberg-valence bound species studied here using collisional charge exchange methods (i.e., in which excited Cs* atoms collide with the molecular cation and transfer an electron to form the neutral).

For all three Rydberg-valence bound species, minimum energy structures, local harmonic vibrational frequencies, and contour representations of their Rydberg-valence bonding orbitals have been given. In addition, the activation barriers separating these structures from their (NH_4) plus alkali hydride fragments as well as the energies required to dissociate to NH_4 plus an alkali atom are reported.

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References and Notes

(1) Boldyrev, A. I.; Simons, J. *J. Phys. Chem*. **1992**, *96*, 8840; *J. Phys. Chem*. **1993**,*97*, 1470.

(2) McMaster, B. N.; Mrozek, J.; Smith, V. H. Chem. Phys. **1982**, 73, 131.

(3) Cardy, H.; Liotard, D.; Dargelos, A.; Poquet, E. *Chem. Phys*. **1983**, *77*, 287. Cardy, H.; Larrieu, L.; Dargelos, A. *Chem. Phys. Lett*. **1986**, *131*, 3874.

(4) Kassab, E.; Evleth, E. M.. *J. Am. Chem. Soc*. **1987**, *109*, 1653.

(5) Talbi, D.; Saxon, R. P. *J. Chem. Phys*. **1989**, *91*, 2376.

(6) Gutowski, M.; Simons, J. *J. Chem. Phys*. **1990**, *93*, 2546, 3874.

(7) Boldyrev, A. I.; Simons, J. *J. Phys. Chem*. **1992**, *97*, 6621.

(8) Simons, J.; Gutowski, M. *Chem. Rev*. **1991**, *91*, 669.

(9) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(10) The $(NH_4)_2^+$ cation was studied earlier by Evleth and coauthors (ref 11), who corrected earlier speculation (Garvey, J. F.; Bernstein, R. B. *Chem. Phys. Lett.* **1988**, *143*, 13) relating to a species claimed to be ammoniated NH_5^+. In so doing, ref 11 offered the first suggestion, accompanied by convincing theoretical calculation, that $(NH_4)_2^+$ is a stable species held together by a one-electron Rydberg bond.

(11) Kassab, E.; Fouquet; Evleth, E. M. *Chem. Phys. Lett*. **1988**, *153*, 522.

(12) Wright, J. S.; McKay, D. *J. Phys. Chem*. **1996**, *100*, 7392.

(13) As noted earlier, when $(NH_4)_2$ fragments to $H_2 + 2NH_3$, 93 kcal/mol is released. In contrast, the one-electron Rydberg-bound $(NH_4)_2^+$ cation is stable with respect to all fragmentation products. Its lowest dissociation path is to $NH_4 + NH_4^+$, which has an energy of 20 kcal/mol. The fragmentations to two $NH_3 + H_2^+$ or to $H_2 + NH_3 + NH_3^+$ occur at significantly higher energies, the latter being the lower of the two and having an endothermicity of 60 kcal/mol.

(14) Boldyrev, A. I.; Simons, J. Proc. Eighth American Conference on Theoretical Chemistry, University of Rochester, Rochester, New York. June 28-July 2, 1993.

(15) McLean, A. D.; Chandler, G. S. *J. Chem. Phys*. **1980**, *72*, 5639.

(16) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem*. **1983**, *4*, 294.

(17) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys*. **1984**, *80*, 3265. (18) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys*. **1980**, *72*, 650.

(18) Cizek, J. *Adv. Chem. Phys*. **1969**, *14*, 35.

(19) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys*. **1982**, *76*, 1910.

(20) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III, *J. Chem. Phys*. **1988**, *89*, 7282.

(21) Schafer, A.; Huber, C.; Ahlrichs, *J. Chem. Phys*. **1994**, *100*, 5829.

(22) Partridge, H.; Bauschlicher, C. W., Jr.; Walch, S. P.; Liu, B. *J. Chem. Phys*. **1983**, *79*, 1866.

(23) Ilyabaev, E.; Kaldor, U. *J. Chem. Phys*. **1993**, *98*, 7126.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chem, W.; Wong, M. W.; Anders, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision A.1; (Gaussian Inc., Pittsburgh, P. A., 1995).

(25) MO pictures were made using MOLDEN3.4 program. Schaftenaar, G. MOLDEN3.4; CAOS/CAMM Center; The Netherlands, 1998.

(26) Cederbaum, L. S. *J. Phys*. **1975**, *B8*, 290.

(27) Niessen, W. von; Shirmer, J.; Cederbaum, J. S. *Comput. Phys. Rep*. **1984**, *1*, 57.

(28) Zakrzewski, V. G.; Niessen, W. von *J. Comput. Chem*. **1993**, *14*, 13.

(29) Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem*. **1995**, *53*, 583.

(30) Ortiz, J. V.; Zakrzewski, V. G.; Dolgunitcheva, O. *In Conceptual Trends in Quantum Chemistry*; Kryachko, E. S., Ed.; Kluver, Dordrecht, 1997; Vol. 3, p 463.